(2)

OFFICE OF NAVAL RESEARCH

CONTRACT N000 14-89-J-1849

R & T Code 4134005

Technical Report No. 5

GROWTH AND CHARACTERIZATION OF GALLIUM(III) OXIDE FILMS

by
P. Wu, Y-M. Gao, R. Kershaw, K. Dwight and A. Wold

Prepared for Publication in

MATERIALS RESEARCH BULLETIN

January 15, 1990

Brown University
Department of Chemistry
Providence, Rhode Island 02912

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT APPROVED FOR PUBLIC RELEASE DISTRIBUTION UNLIMITED
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) # 5	5. MONITORING ORGANIZATION REPORT NUMBER(S) N000 14-89-J-1849
6a. NAME OF PERFORMING ORGANIZATION BROWN UNIVERSITY AARON WOLD 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION OFFICE OF NAVAL RESEARCH
6c. ADDRESS (City, State, and ZIP Code) DEPARTMENT OF CHEMISTRY BROWN UNIVERSITY PROVIDENCE, RI 02912	7b. ADDRESS (City, State, and ZIP Code) 800 N. Quincy St. Arlington, VA 22217
8a. NAME OF FUNDING/SPONSORING ORGANIZATION 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO / PROJECT NO / TASK NO / WORK UNIT NO

11. TITLE (Include Security Classification)
GROWTH AND CHARACTERIZATION OF GALLIUM(III) OXIDE FILMS

12. PERSONAL AUTHOR(S)
P. wu, Y-M. Gao, R. Kershaw, K. Dwight and A. Wold

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM _____ TO _____	Jan 15, 1990	7

16. SUPPLEMENTARY NOTATION
PREPARED FOR PUBLICATION IN MATERIALS RESEARCH BULLETIN

17 COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A simple spray pyrolysis technique has been applied to the formation of dense, homogeneous gallium(III) oxide thin films on both silicon and silica substrates. The high quality of these films has been established by transmission electron microscopy, x-ray diffraction, optical spectra, and current-voltage measurements.

Keywords:
Gallium compounds; Thin films; (AW)

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code) / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

GROWTH AND CHARACTERIZATION OF GALLIUM (III) OXIDE FILMS

P. Wu, Y-M. Gao, R. Kershaw, K. Dwight and A. Wold

Department of Chemistry, Brown University
Providence, RI 02912

ABSTRACT

A simple spray pyrolysis technique has been applied to the formation of dense, homogeneous gallium(III) oxide thin films on both silicon and silica substrates. The high quality of these films has been established by transmission electron microscopy, x-ray diffraction, optical spectra, and current-voltage measurements. MATERIALS INDEX: Gallium(III) oxide; Thin films.

Introduction

Gallium(III) oxide can exist in several different structures, namely α, β, γ, δ, and ε (1). Of the five modifications, the β form is the most stable from room temperature to the melting point (1795°C). β-Ga_2O_3, with a monoclinic structure (space group A2/m), is a semiconductor with a band gap of 4.8 eV (2). Its hardness is 9.0 on the Mohs' scale (3). Kim, et al, reported the growth of polycrystalline Ga_2O_3 thin films (4). The films were grown by spraying a $GaCl_3$ solution onto borosilicate glass substrates. The band gap of the films was measured; however, the film quality was not analyzed.

Recently, a novel ultrasonic nebulization and pyrolysis technique has been developed in this laboratory for the preparation of thin oxide films of high quality (5,6). This paper reports on the preparation of gallium oxide thin films by this simple method. The structural, optical and electrical properties of the films are also investigated.

Experimental

Solution Preparation

A solution was prepared by dissolving 4.24 g of $Ga(NO_3)_3 \cdot xH_2O$ (Strem) in 10 ml of distilled water and 1 ml of methanol. This solution was immersed in an ice bath with constant stirring and 4 ml of acetylacetone (Aldrich) and 4 ml of propylene oxide (Aldrich) were added. Next, 4 ml of concentrated

ammonium hydroxide were added to the solution and a fluffy white precipitate was formed. The precipitate and solution were refrigerated overnight and filtered. The precipitate was washed with hexane and air dried. The product was dissolved in 0.3 M acetic acid resulting in a solution which was 0.02 M in Ga^{3+}.

Preparation of Ga_2O_3 Films

Gallium oxide films have been prepared by an ultrasonic nebulization and pyrolysis technique developed in this laboratory (5). The reactor used in this investigation is shown in Fig. 1, and it was heated by a two-zone mirror furnace (Transtemp Co., Chelsea, MA). A mixed solution of gallium acetylacetonate and acetic acid was nebulized by a commercial ultrasonic humidifier (Holmes Air) and was carried into a horizontal reactor by oxygen. The substrate was held perpendicular to the gas flow in the furnace by a silica holder which was rotated by a low speed motor to achieve best uniformity. Both the efficiency of the deposition and the uniformity of the films were affected by the deposition parameters used. Typical reaction parameters were: furnace temperature, 450°C; oxygen flow rate, 3.7 liter/min; distance between nozzle and substrate, 77 mm. Under such conditions, a film of 2000 Å could be grown in 40 minutes using 13 ml of solution. Both silicon and silica wafers were used as substrates. Cleaning of the silicon substrates was carried out just prior to the deposition according to the procedure described by Fournier et al. (7). Silica substrates were cleaned with hydrochloric acid, distilled water and semiconductor grade acetone prior to the deposition.

Film Characterization

The thickness of the films on silicon substrates was determined by ellipsometry using a Rudolph Research Auto EL-II ellipsometer (8), whereas those on silica substrates were measured by interference fringes in their UV-visible spectra.

X-ray diffraction patterns of the gallium oxide films were obtained using a Philips diffractometer and monochromated high intensity $CuK\alpha_1$ radiation (λ = 1.5405 Å). Diffraction patterns were taken with a scan rate of 1° 2θ/min over the range 20° < 2θ < 65°.

Characterization of the surface topography of films deposited on silicon was achieved by examining replicas of the surface in a transmission electron microscope. A replication solution (Ladd) was applied to the surface of the film and allowed to dry. The plastic formed a negative image of the surface. A carbon-platinum pellet was shadow-evaporated onto the stripped plastic at a glancing angle followed by a uniform layer of carbon. The carbon replicas were liberated using acetone, mounted on 200 mesh copper grids and examined in a Philips 420 Scanning Transmission Electron Microscope (STEM) operating at 20 KV.

Optical measurements of the films on silica substrates were performed using a Cary model 17 dual beam ratio recording spectrophotometer in the range of 200 to 1200 nm. Measurements were made in the transmission mode. The optical band gap was deduced from the transmittance near the absorption edge. The thickness of each film was obtained from the fringes in the spectra.

Current-voltage measurements were performed to determine the DC breakdown voltage of the films. Both $Au/Ga_2O_3/Si$ and $Au/Ga_2O_3/Au$ configurations were used. Gold was evaporated through a mask to obtain an

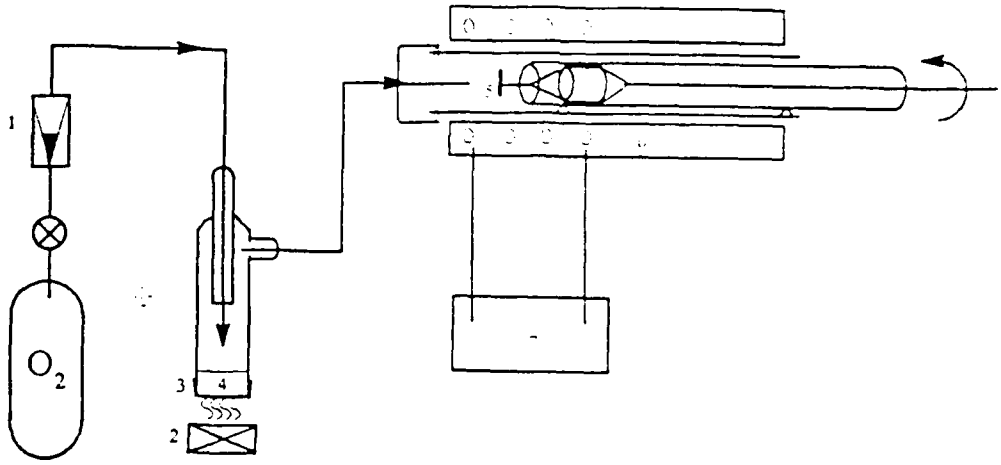
array of circular electrodes on the surface of the gallium oxide film of area 1 mm^2. Contact to a gold dot electrode was obtained by touching a gold-tipped micromanipulator to the surface. With the configuration $Au/Ga_2O_3/Si$, contacts to the silicon substrates (n-type with a resistivity of 0.01 Ω-cm) consisted of indium alloy (Indalloy 9, Indium Corporation of America) ultrasonically bonded to the back surface. The indium alloy contacts were checked for ohmic behavior before measurement of the current-voltage behavior. To obtain the $Au/Ga_2O_3/Au$ configuration, a gold strip was evaporated onto the surface of the silicon substrates before film preparation. Part of the gold surface was masked during the film deposition and contact was made to the gold electrodes on both sides of the film. The reported current-voltage behavior is that for the gold dot electrode made negative with respect to the substrate. The area measured ignores a 1 mm boundary along the substrate edge. A DC potential was applied via a voltage follower having an output impedance less than 0.1 Ω, and the resulting response was measured with a current amplifier, which inserted a negligible potential drop (less than 1 microvolt) in the external circuit.

Results and Discussion

Smooth and homogeneous gallium oxide films have been grown on both silicon and silica substrates using an ultrasonic nebulization and pyrolysis technique. The films had good adherence to both substrates. They appeared uniform and shiny with bright colors varying with the thickness. The thickness of a number of films on silicon substrates was measured at different positions on the films with an ellipsometer, and was found to be uniform to within 1% on a substrate of 1 x 1 cm^2, except near the very edge. The bright and uniform color also revealed that the films were of uniform thickness.

Kamata (9) reported that gallium acetylacetonate (volatization temperature = 150°C) can be used as a source material for chemical vapor deposition of oxide films. Under the reaction conditions of this study (450°C), the fine mist of gallium complex solution could dry and volatilize before it decomposed. The films would then be deposited from the vapor phase of the source material. Therefore, the mechanism of this kind of film deposition is probably a CVD-like process. This is consistent with the probable volatility of the gallium acetylacetonate complex in dilute acetic acid solution. The smooth, shiny and mirror-like appearance of the Ga_2O_3 films grown in this study suggested that they were probably deposited from a vapor phase. Viguie and Spitz (10) discussed the mechanism in a similar process and they concluded that the best films were obtained when the source material volatilized and the vapor deposited directly on the substrate. Based on the previous study of the formation of Al_2O_3 films from aluminium acetylacetonate solution (11), it was concluded that the gallium complex probably contains acetylacetanato ligands and that some of these ligands have been replaced by water and/or acetate ion.

The films prepared by the above method were analyzed by x-ray diffraction. Fig. 2 shows the x-ray diffraction patterns of a film of 0.5 μm in thickness both as-deposited at 450°C and after annealing at 800°C for six hours in flowing oxygen. The diffraction pattern of the as-deposited film is featureless and represents the amorphous nature of the film. In the pattern of the film after annealing, all peaks correspond to the reflections of the β-Ga_2O_3 phase. A photomicrograph of a carbon replica of an as-deposited gallium oxide film of 0.3 μm on silicon is shown in Fig. 3. There is a uniform grain texture that can be observed in the picture, with grain sizes of about 0.1 μm.



1. Flowmeter
2. Ultrasonic Supply
3. Membrane
4. Solution
5. Substrate
6. Furnace
7. Temperature Controller

Fig. 1. Schematic diagram of the deposition apparatus

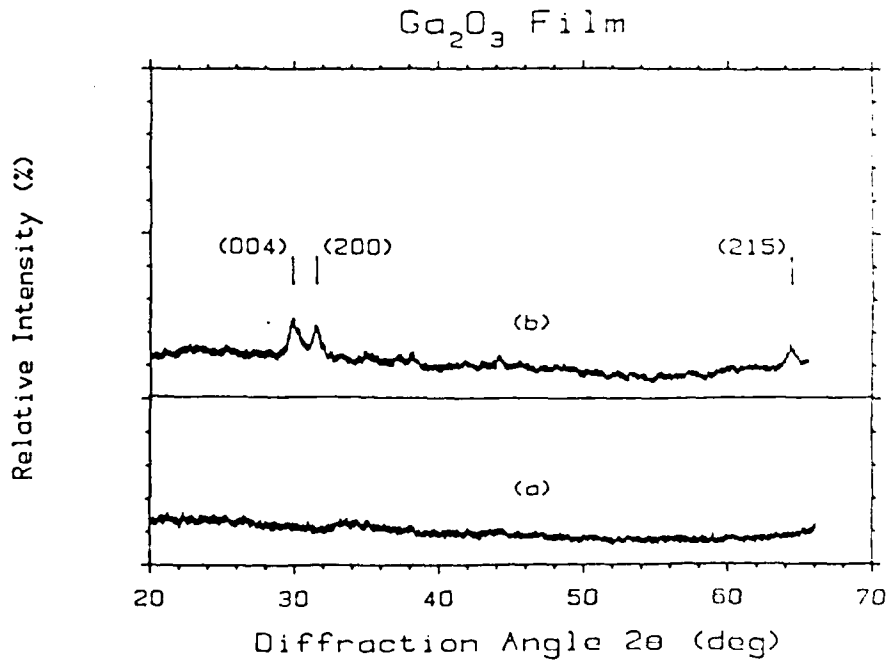


Fig. 2. X-ray diffraction patterns of a Ga_2O_3 film of 0.5 μm (a) as deposited; (b) after annealing at 800°C for 6 hrs.

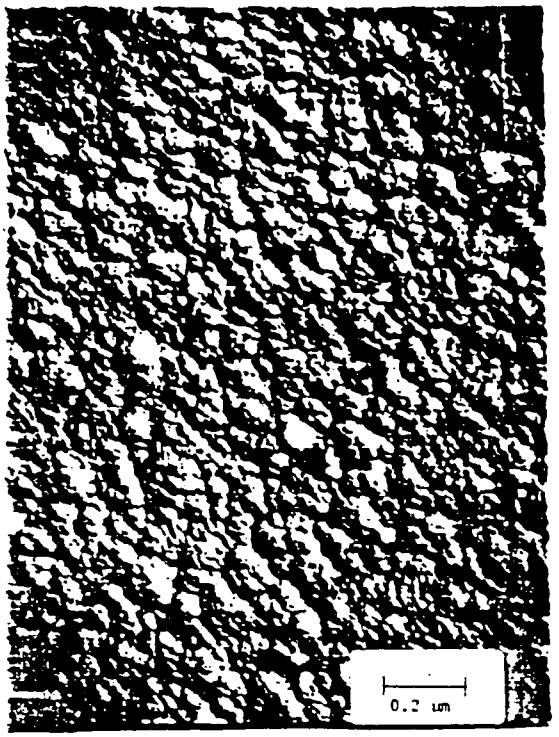


Fig. 3. Micrograph of a gallium oxide film of 0.3 µm thickness.

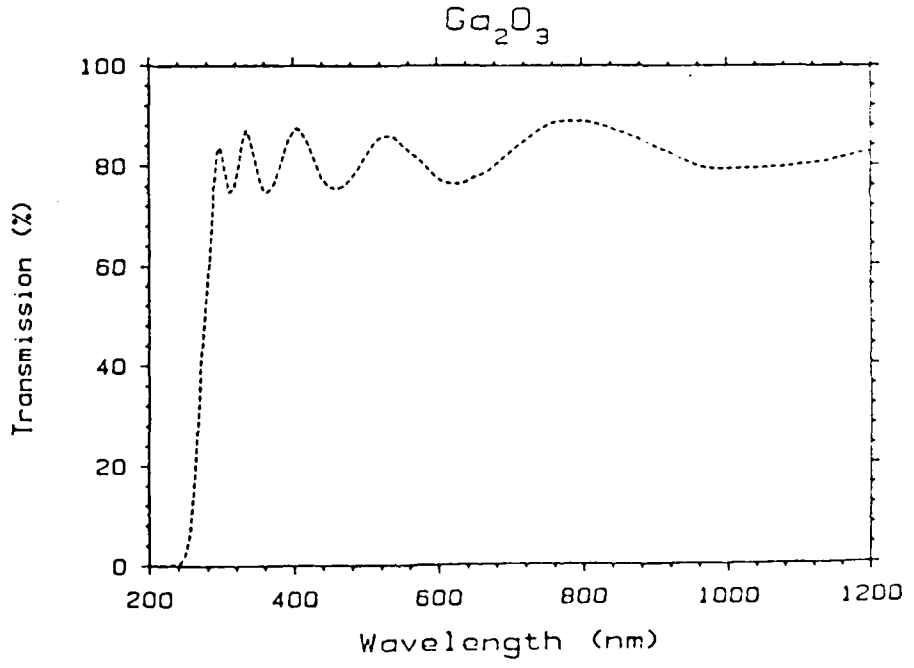


Fig. 4. Transmission spectrum of a gallium oxide film on silica.

The transmission spectrum of a gallium oxide film on silica is shown in Fig. 4. The optical absorption derived from such data was used to generate plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$, which gave a band-gap energy of 4.79 eV. This result is in agreement with the value reported in the literature (12).

Current-voltage measurements were made on several films approximately 2000 Å thick in both $Au/Ga_2O_3/Si$ and $Au/Ga_2O_3/Au$ configurations. There was no observed voltage breakdown up to 10 V applied DC potential in either case. This indicated that the films are dense and potentially useful as insulating layers.

Conclusions

Gallium oxide films were prepared by an ultrasonic nebulization and pyrolysis method using gallium acetylacetonate as source material. Homogeneous, uniform films with good adherence have been obtained using this simple technique. The films are amorphous and will crystallize into β-Ga_2O_3 with annealing. These films are transparent and have submicron grain texture with a band gap value of 4.79 eV. It appears that the ultrasonic nebulization technique can give homogeneous, uniform films of high quality as a result of the oxide being deposited from the vapor phase. This is in contrast to spraying a liquid onto the surface of a substrate, which almost always results in poor, porous films.

Acknowledgments

This research was partially supported by the Office of Naval Research and by the National Science Foundation DMR 8901270 and DMR 8803184. Partial support was also received from the Eastman Kodak Company, Rochester, NY and GTE Labs, Inc., Waltham, MA.

References

1. R. Roy, V.G. Hill and E.F. Osborn, *J. Am. Chem. Soc.*, 74, 719 (1952).

2. M.R. Lorenz, J.F.Woods and R.J. Gambino, *J. Phys. Chem. Solids*, 28, 403 (1967).

3. "The Oxide Handbook," G.V. Samsonov, Ed.; Plenum Data Corporation: New York, 1973, p. 255.

4. H-G. Kim, W-T. Kim, *J. Appl. Phys.*, 62, 2000 (1987).

5. P. Wu, Y-M. Gao, J. Baglio, R. Kershaw, K. Dwight and A. Wold, *Mat. Res. Bull.*, 24, 905 (1989).

6. W. DeSisto, M. Sosnowski, F. Smith, J. Deluca, R. Kershaw, K. Dwight and A. Wold, *Mat. Res. Bull.*, 24, 753 (1989).

7. J. Fournier, W. DeSisto, R. Brusasco, M. Sosnowski, R. Kershaw J. Baglio, K. Dwight and A. Wold, *Mat. Res. Bull.*, 23, 31 (1988).

8. R. Brusasco, R. Kershaw, J. Baglio, K. Dwight and A. Wold, *Mat. Res. Bull.*, 21, 301 (1986).

9. K. Kamata, European Patent Application EP 55459, 1982. Chem. Abstr., 97:154373.

10. J. C. Viguie and J. Spitz, *J. Electrochem. Soc.*, 122, 585 (1975).

11. W. J. DeSisto, Y-T Qian, C. Hannigan, J.O. Edwards, R. Kershaw, K. Dwight and A. Wold, To be submitted to Mat. Res. Bull.

12. H. H. Tippins, *Phys. Rev.*, 140, A316 (1965).